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A STUDY OF THE DETERIORATION OF NICKEL SPARK-PLUG ELECTRODES IN SERVICE

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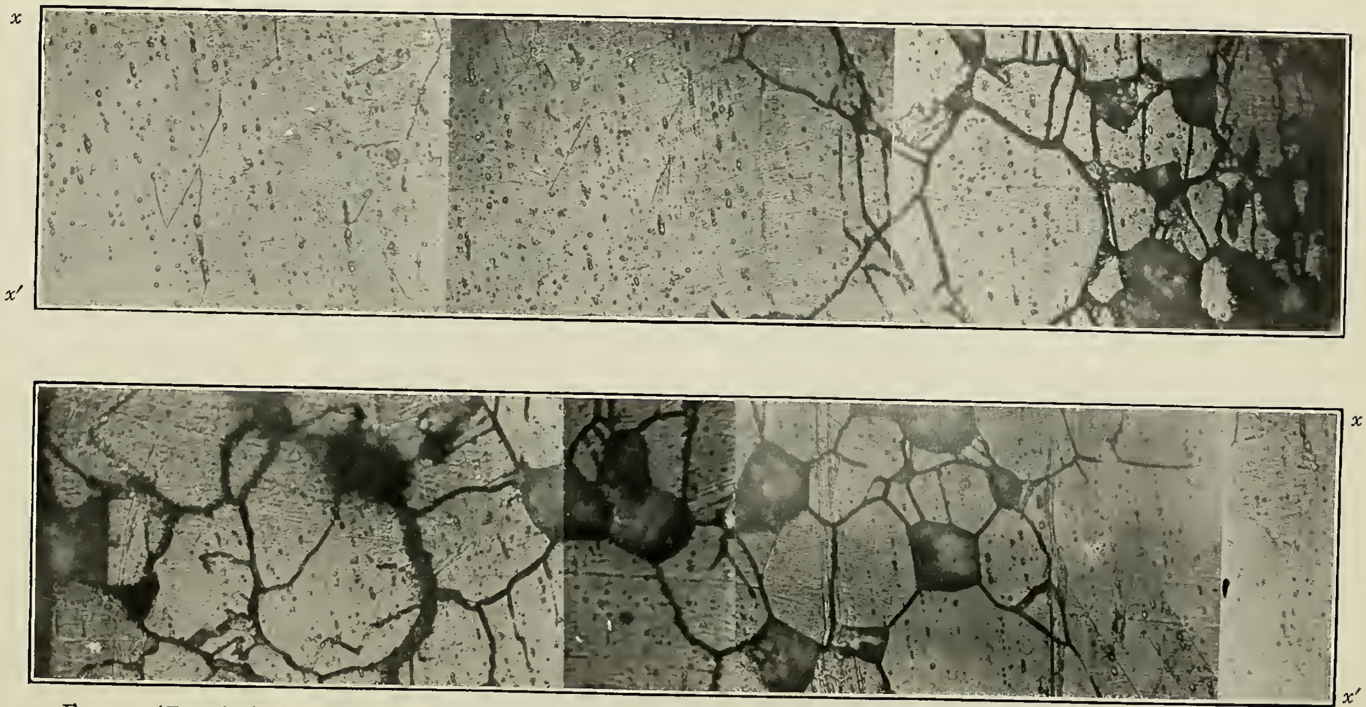


FIG. 1.—(*Frontispiece.*) *Deterioration of nickel electrodes: Medial longitudinal section through a nickel side electrode of a spark plug after deterioration*

The etching develops intercrystalline fissures in the outer layers; some of the crystals have loosened and dropped out of place. Magnification, originally 500 diameters; reduced to 385 in reproduction. Etching, concentrated nitric acid, five seconds

A STUDY OF THE DETERIORATION OF NICKEL SPARK-PLUG ELECTRODES IN SERVICE

By Henry S. Rawdon and A. I. Krynitzky

CONTENTS

I. INTRODUCTION

The most commonly used material for electrodes in spark plugs is commercial nickel wire. The relatively high temperature of melting, its excellent heat conductivity, and the slow rate at which the metal is oxidized, even upon continued heating at high temperatures, are the principal determining factors in the choice of nickel for this purpose. The grade of nickel wire commonly used for the electrodes averages 97 per cent nickel, the remainder being manganese, cobalt, iron, and copper, with traces of other impurities always found in commercial nickel.

A peculiar and interesting type of deterioration which occurs in these nickel electrodes during the service life of the spark plug has recently been brought to the attention of the Bureau of Standards. Commercial spark plugs vary greatly in their size and shape, and the electrodes likewise differ considerably as to their relative size, shape, number, and arrangement with respect to each other.

CORRECTIONS

Table 2, read .09 (for .00)
Fig. 11, interchange "b" and "c"
Figs. 15 and 16, omit "original".

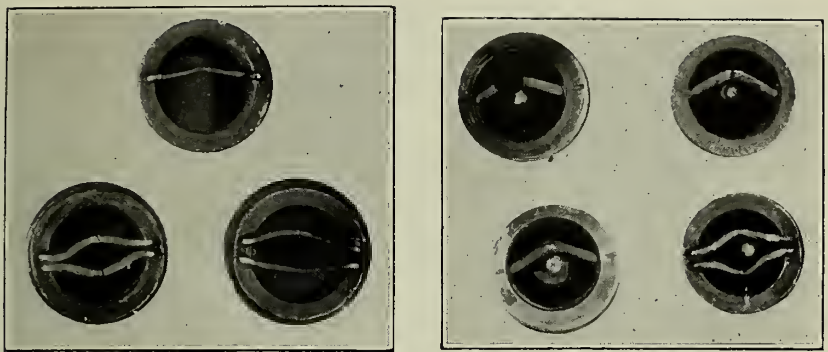
Although this defect was studied in detail in only one of the many varied forms of spark plugs, it became evident from the examination that the deterioration is a characteristic of the material—that is, of nickel wire—rather than of the particular type of spark plug in which it was noted and studied. It appears, however, that the mechanical features of the plugs have a considerable bearing on the time required for the deterioration to become serious. The results of this study of the deterioration of nickel electrodes in service should be of value to the makers of all types of spark plugs in which the electrodes are made of this metal.

II. CHARACTER OF DETERIORATION OF WIRES DURING SERVICE

1. APPEARANCE AND PROPERTIES OF THE CHANGED WIRE

The nickel electrodes in which the deterioration was studied were taken from spark plugs in which the electrodes are arranged as a central one with the ground or side electrode attached firmly at both ends to the shell of the plug. In some of the plugs two side electrodes were used, one on each side of the central one. Although both electrodes were found to have deteriorated to some extent, the attack of the central one was quite negligible as compared to that of the side ones. These latter wires had developed in service transverse cracks which in many cases were as sharp and definite as a knife cut. After a separation occurred, the breach widened by loss of material from the ends of the fractured wires until a gap of as much as 1 cm often resulted. Fig. 2 shows the appearance of some of the side electrodes in different stages of deterioration. In Fig. 3 is shown the appearance of the surface of the side electrodes after removal of the carbonaceous deposit which usually covers them. The surface is roughened by a series of parallel transverse cracks; none of these, however, has penetrated deeply enough to cause a break of the wire. In general, these transverse cracks occur more frequently on the side of the electrode on which most of the "sparking" occurs—that is, the one facing the central electrode—than on the farther side. The central electrode shows no appreciable change other than a slight roughening of the tip.

The appearance of the fracture of the side electrodes is that of very brittle material, there being no elongation and no reduction of cross-sectional area. The face of the fracture itself is rough and crystalline. The mechanical properties of three samples of



a b

FIG. 2.—*Service breaks in nickel electrodes: View, slightly reduced, of the end of spark plugs to show the fracture in the side electrodes; a and b represent two different grades of nickel wire*

FIG. 3.—*Surface changes in nickel electrodes: View of surface of side electrode after considerable service, showing the transverse cracks which develop. Magnification, 3 diameters*

new wire said by the manufacturers to be of the same stock as the failed electrodes were determined with the results shown in Table 1.

TABLE 1.—Mechanical Properties of Nickel Wire

Specimen	Character of wire	Ultimate strength	Elongation in— 8-inch gage length	Elongation in— 2-inch gage length
		Lbs./in.	Per cent.	Per cent.
1	Hard-drawn	110 000	(a)	(a)
2	Annealed	73 000	26	30
3	do	78 500	29	31
4	do	65 200		28

a Not determined; very small.

Specimen 1 was said to be the material from which the failed electrodes of Fig. 2, *a*, were made and resembles it quite closely. (See Table 2.) The electrodes shown in Fig, 2, *b*, which were said to have been made from wire similar to specimens 2 and 3, evidently were made from wire quite similar in composition to specimen 4 (see Table 2), though not necessarily of the same mechanical properties.

Specimen 4 is a sample of annealed nickel wire from the Bureau of Standards stock; this material was used in all the experimental work described later (Sec. III).

The fragments of the deteriorated wire electrodes removed from the spark plugs were found on the whole to be rather ductile and to stand several sharp right-angle bends before breaking. The extreme end portion immediately adjacent to the break, however, was brittle and broke readily when an attempt was made to bend it.

An explanation of the embrittlement of nickel wires used for the winding of an electric furnace has been offered by Carpenter.[1] This assumes the presence within the metal of occluded gas, which is liberated under the combined action of electricity and heat. The wires described by Carpenter separated into a bundle of long thin threads after considerable use of the furnace. The explanation does not answer in the present case, in which the wires are always fractured by a series of transverse cracks.

[1] H. C. H. Carpenter, Collected Researches, 3, National Physical Laboratory, Teddington.

2. CHEMICAL COMPOSITION

Both the deteriorated electrodes and samples of unused wires were analyzed chemically. The results are summarized in Table 2.

TABLE 2.—Chemical Composition of Commercial Nickel Wire

Specimen	Nickel	Cobalt	Copper	Silicon	Manganese	Iron
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
(a) Failed wires Fig. 2, a	97.3	(a)	0.1	0.4	1.5	0.5
	97.2	(a)	.1	.4	1.5	.5
(b) Failed wires, Fig. 2, b	99.0	(a)	.1	.4	.05	.4
	99.1	(a)	.1	.4	.05	.4
(c) 1, Table 1	97.1	0.7	.14	.12	1.3	.6
(d) 2, Table 1	96.9	.3	.09	.25	1.6	.8
(e) 3, Table 1	97.1	.3	.00	.18	1.5	.8
(f) 4, Table 1	98.1	1.1	.18	.07	.2	.3

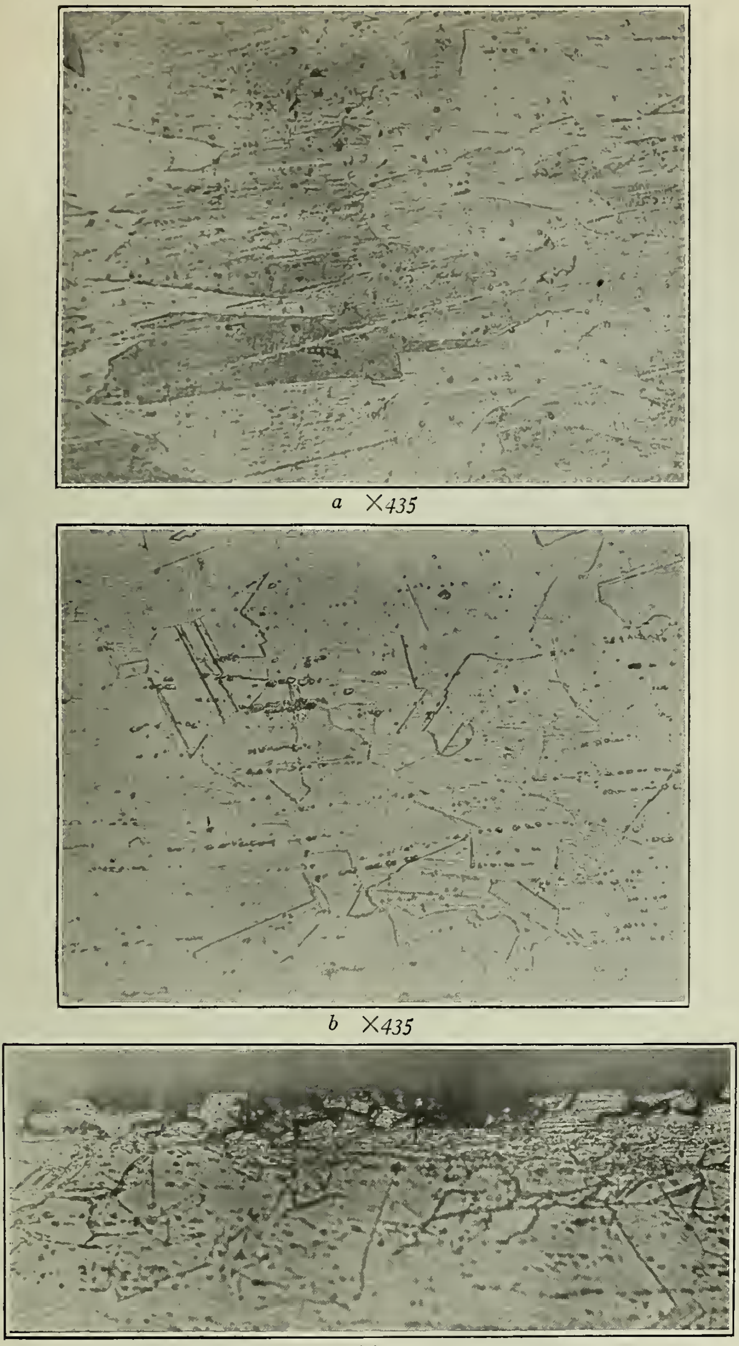
[a] Cobalt was not determined; it is included with nickel.

It will be noted from the results that deterioration occurs in both the usual 97 per cent grade of nickel wire with relatively high manganese content and in the wire of higher nickel content.

3. MICROSTRUCTURE OF COMMERCIAL NICKEL WIRE

In Fig. 4 is shown the microstructure of commercial nickel wire in the hard-drawn and in the annealed state (specimens 1 and 4, respectively, Table 1). The metal consists of but one type of crystals, as is true with pure metals and solid solutions in general. In the hard cold-drawn wire the crystals show the results of the severe distortion due to the drawing by their elongated form; upon annealing sufficiently a recrystallization takes place and the characteristic appearance shown in Fig. 4, *b*, results. The minute inclusions of oxide and other impurities, which have been arranged in lines parallel to the direction of working during the drawing operation, have been dissolved by the strong etching solution (concentrated nitric acid) which is necessary to develop satisfactorily the crystalline structure of nickel. A definite etching pit marking the location of each inclusion results.

Fig. 4, *c*, shows the outer surface of the annealed nickel wire of Fig. 4, *b*, This wire has received no treatment after the final annealing by the manufacturers. In an extremely thin outer layer a structural change very similar to that which occurs in the nickel electrodes during service has taken place. This undoubtedly occurred during the final annealing; the hard-drawn wires showed



a ×435

b ×435

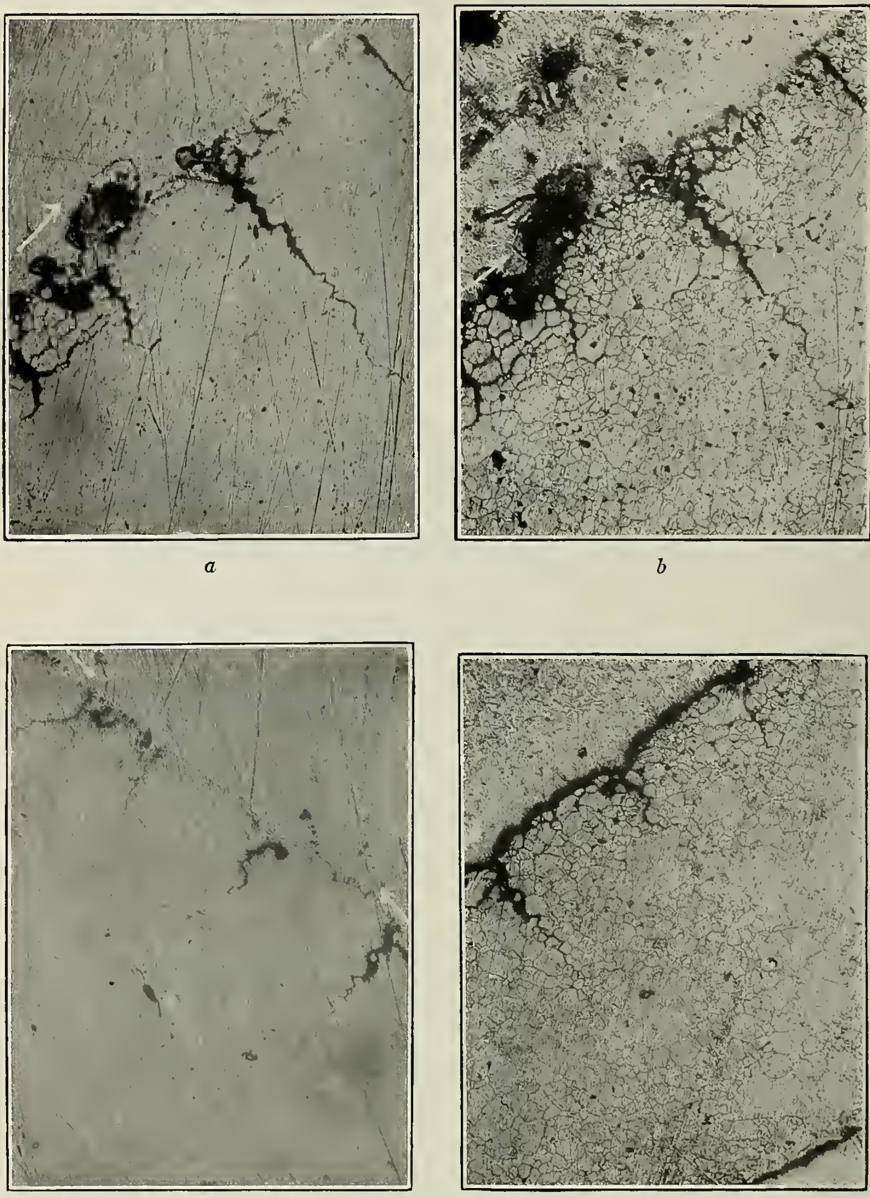
c ×417

Fig. 4.—*Commercial nickel wire: Microstructure of wire of the grade used as spark-plug electrodes*

a, Longitudinal section of hard-drawn wire; *b*, longitudinal section of annealed wire; *c*, edge of section shown in *b*, i. e., the surface of the wire

Intercrystalline fissures appear in a very thin surface layer of metal; these have probably formed during the final annealing of the wire

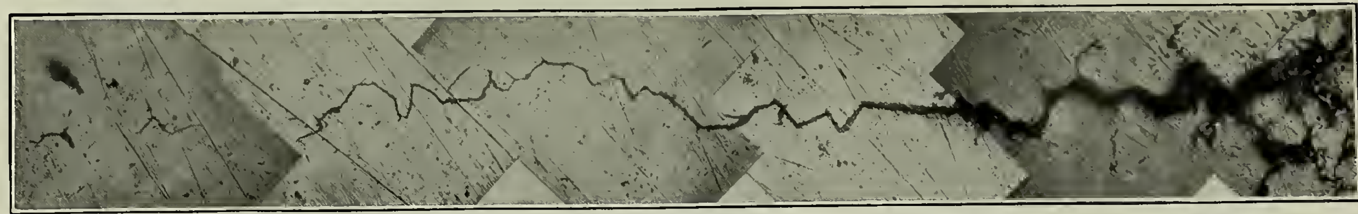
Original magnification, 500 diameters; reduced as indicated in reproduction. Etching, concentrated nitric acid. five seconds



a b c d

FIG. 5.—*Service deterioration of nickel electrodes: Longitudinal sections of side electrodes showing deterioration in service; the arrows indicate the edge of the nickel wire*

a, Unetched specimen; *b*, specimen *a* after etching; *c*, unetched specimen; *d*, specimen *c* after etching. Original magnification, 100 diameters; reduced to 72 in reproduction. Etching, concentrated nitric acid, one to two seconds

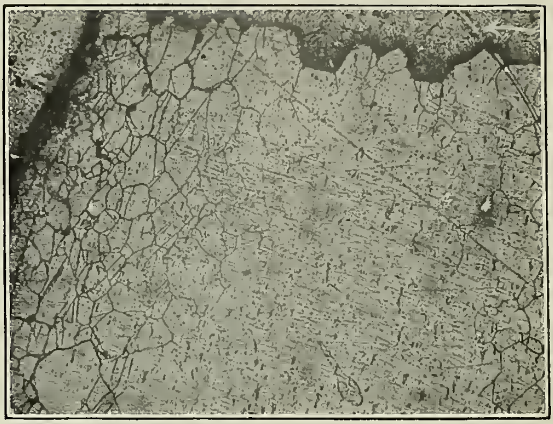


a

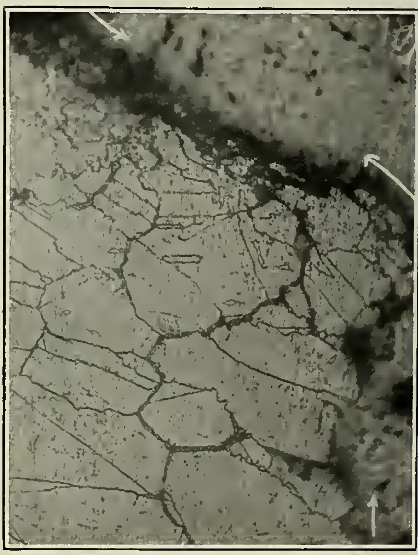
b

FIG. 6.—*Service deterioration of nickel electrodes: Longitudinal section of a side electrode showing one of the transverse cracks of Fig. 5, d*

a, Unetched; *b*, etched, one to two seconds, with concentrated nitric acid
Original magnification, 500 diameters; reduced to 220 diameters in reproduction



a



b *c*

FIG. 7.—*Nature of deterioration of nickel electrodes: Longitudinal section through fractured end of wire*

a, Section showing the network in the outer zone of the wire and also the intercrystalline fracture. Original magnification, 200 diameters; reduced to 143 in reproduction; *b* and *c* show the lower left-hand corner before and after etching. Original magnification, 500 diameters; reduced to 357 in reproduction. Some of the intercrystalline fissures show a gray nonmetallic substance, evidently oxide. Etching, concentrated nitric acid, one to two seconds

no trace of such a change in the surface metal. In the following discussion (Sec. III) of structural changes produced experimentally in the nickel wire, it should be borne in mind that the extreme surface layer has already been changed to the extent shown in Fig. 4, *c*.

4. MICROSTRUCTURAL CHANGES PRODUCED DURING SERVICE

Longitudinal sections of the deteriorated side electrodes were prepared for microscopic examination. The small fragments of the wire were plated with a heavy deposit of electrolytic copper to preserve the edges of the section during the process of polishing; the coated piece was then mounted in a suitable matrix and the resulting composite specimen sectioned and polished. In most of the micrographs a portion of the protective layer of copper appears immediately adjacent to the edge of the section of the nickel wire.

In Fig. 5 is shown the appearance of longitudinal sections of the side electrode. A series of parallel transverse cracks, some of which extend very deeply into the otherwise sound metal, is apparent in the unetched specimen. By etching with concentrated nitric acid for several seconds, the crystal boundaries of the metal are revealed and the intercrystalline nature of the transverse cracks is made evident. Fig. 6, *a* and *b*, shows the course of one of these cracks at a relatively high magnification.

In addition to the intercrystalline transverse cracks which penetrate deeply into the metal, the microscopic examination revealed a zone on the outside of the wire in which the crystal boundaries etch very readily, forming a complete network of intercrystalline fissures; in some cases entire crystals become detached in this zone and fall bodily out of place. These features are shown in Fig. 1, frontispiece, which gives a narrow transverse section entirely across one of the side electrodes.

In Fig. 7, *a*, *b*, and *c*, is shown a portion of one of the side electrodes adjacent to the fracture which occurred in this wire. The break was distinctly intercrystalline, as is to be expected from the nature of the transverse cracks. Before etching, many of the intercrystalline fissures are seen to contain a film of gray nonmetallic substance. This is shown in Fig. 7, *b* and *c*. In Fig. 9 the intercrystalline eutecticlike network, seen in the outer portions of the deteriorated wires, is shown. This appears in the unetched specimen.

Fig. 8 shows a section through the fracture of one of the broken side electrodes and clearly shows the intercrystalline path of the fracture together with some of the sound unchanged metal just back of the face of the break.

The examination of the central electrode showed that a change of the same general character as occurred in side electrodes had taken place in this one, also, but to a slighter degree. In a zone of metal which covers the upper end of the electrode like a cap, the intercrystalline network is well developed. This cap was found in some electrodes to be approximately 0.3 mm (0.012 inch) thick at the tip and to extend as a layer of constantly decreasing thickness for approximately 15 mm (5/8 inch) along the length of the electrode. In the same specimen the side electrode had fractured and a gap of over 7 mm width had formed. In Fig. 10 the general extent of the deterioration of the central electrode is shown. In no case were any of the definite transverse cracks which were noted in the side electrodes found in the central one. Tiny fissures gradually form in the attacked metal which caps the end of the electrode, and groups of crystals become detached, thus gradually shortening the electrode. The relative intensity of the attack in the central and in the side electrodes is shown in Fig. 11. A section of a cross section of the top of a central electrode, the fractured end of a side electrode, and the cool end of the same fragment (that is, the end attached to the shell of the plug) shows the depth of the zone of deterioration in each case.

To illustrate the service behavior of side electrodes anchored at only one end, a number of spark plugs of a different type were examined. These had been used for various periods in a 'Liberty' motor. The side electrodes in this plug are bent at a right angle, fastened to the shell at one end, and terminate near the tip of the central electrode which is of nickel wire of the same size as the side electrodes. Both electrodes in this case show the same type of deterioration as was found in the central electrode of the plugs previously examined; that is, a cap of metal in which the intercrystalline fissures are well developed covers the free end of each. Fig. 12, *a* and *b*, shows the appearance of the two. In none of the electrodes, side or central, were any of the deep transverse cracks found. The plugs had been subjected to a continuous service which varied in the different plugs from 9¾ to 28 hours. The thickness of the zone of deteriorated metal in the electrodes which have had the longest service does not differ

FIG. 8.—*Nature of the fracture of the deteriorated wire: Longitudinal section through the fractured end of a broken electrode*

The path of the fracture is truly intercrystalline; the unchanged sound metal appears just back of the break. Original magnification, 500 diameters; reduced to 263 in reproduction. Etching, concentrated nitric acid, five seconds

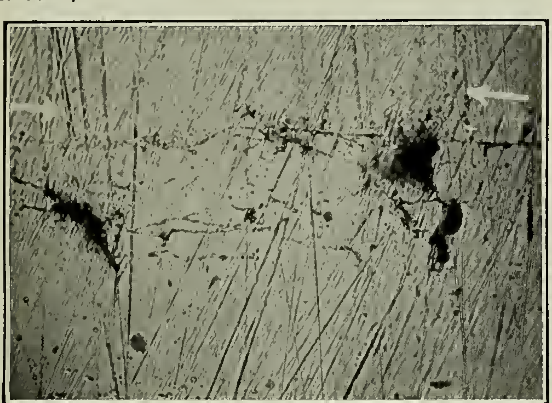


FIG. 9.—*Nature of deterioration: Longitudinal section of a side electrode deteriorated in service, unetched*

A eutecticlike network forms between the crystals in the outer zone of the wire. The arrows indicate the edge of the section of the wire. Magnification, 500 diameters

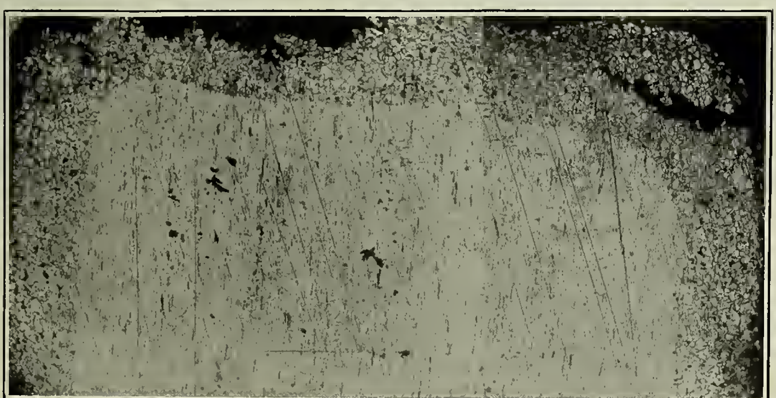
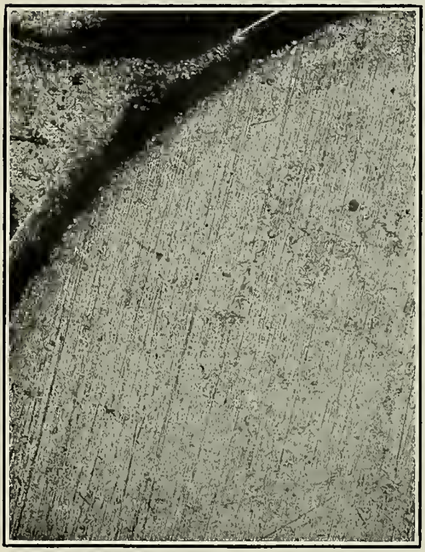


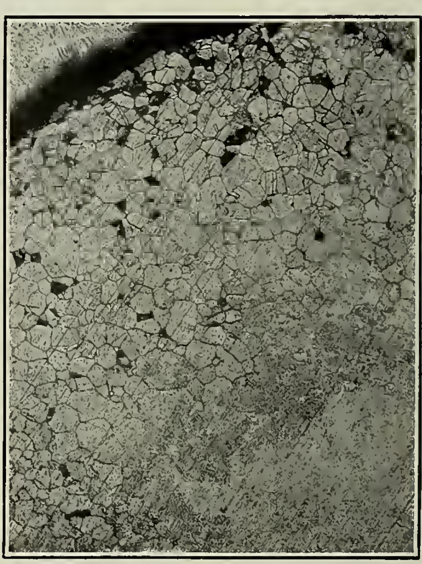
FIG. 10.—*Deterioration of central electrode: Longitudinal section through the tip of the central electrode to show the extent of the deterioration*

A thin layer which entirely caps the upper end has been affected. Original magnification, 75 diameters; reduced to 44 in reproduction. Etching, concentrated nitric acid, one to two seconds

a ×77



b ×72

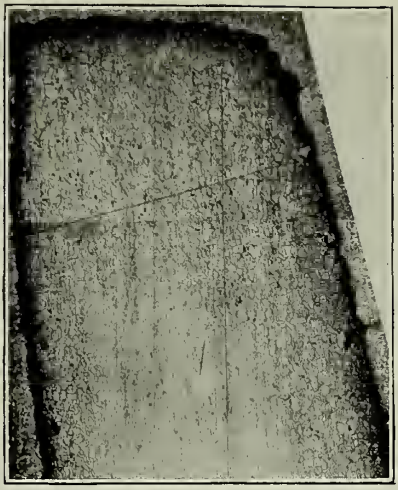


c ×72

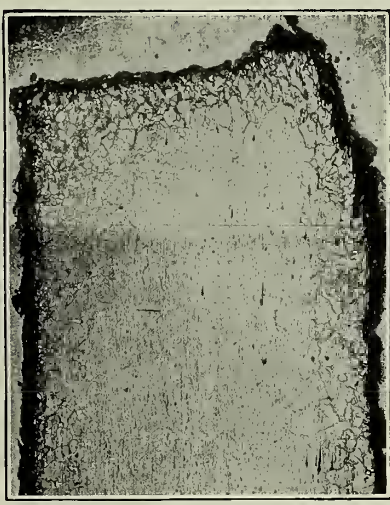
FIG. 11.—*Relative deterioration of central and side electrodes*

a, Portion of a cross section of the upper tip of the central electrode; *b*, portion of a cross section just back of the fracture of a side electrode; *c*, portion of a cross section of the opposite end of *b*; that is, where the electrode is attached to the plug shell (cool end)

The center of the wire corresponds quite closely in each case with the lower corner of the micrographs. Original magnification, 100 diameters; reduced as indicated in reproduction



a

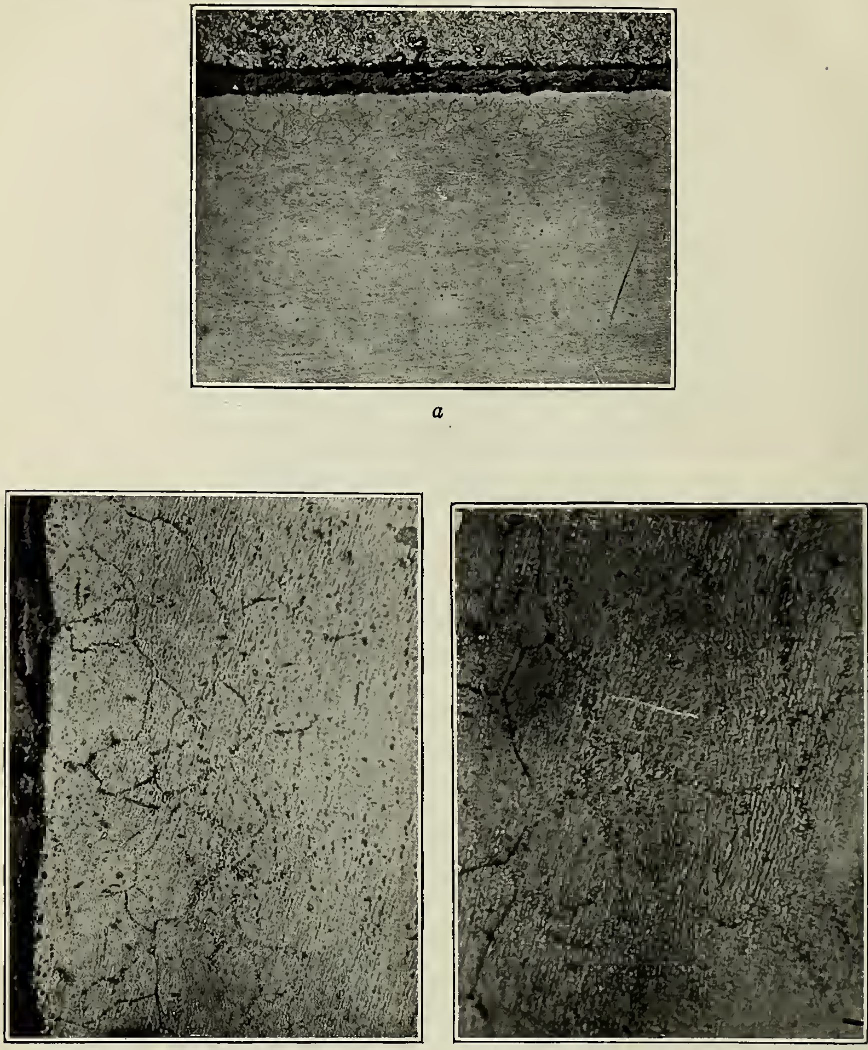


b

FIG. 12.—*Electrodes from spark plugs in which the side electrode is anchored at only one end removed after nine hours' service in Liberty motor*

a, Longitudinal section of the free (hot) end of the side electrode; *b*, longitudinal section of the tip of the central electrode

Original magnification, 75 diameters; reduced to 34 in reproduction. Etching, concentrated nitric acid, two seconds.



a

b c

FIG. 13.—*Influence of oxidation upon nickel wires: Longitudinal section of a specimen heated 120 hours, 48 hours at approximately 750° C., 72 hours at approximately 870° C. (Specimen 12, a, Table III)*

A definite eutecticlike intercrystalline network has formed in the metal just beneath the heavy oxide layer

a, Original magnification, 100 diameters, reduced to 67 in reproduction; *b*, original magnification, 500 diameters, reduced to 385 in reproduction; *c*, original magnification, 1000 diameters, reduced to 735 in reproduction

The network as it first forms is granular in appearance; later a complete film is formed. Etching, concentrated nitric acid, one second

markedly from that of electrodes of the shorter service. The loss of surface metal from the tip of the wires during service in part explains the rather striking uniformity in thickness of the cap of deteriorated metal.

III. POSSIBLE FACTORS CONTRIBUTING TO THE DETERIORATION

1. CHEMICAL COMPOSITION

From the results of Table 2 it is evident that variations in chemical composition such as occur in commercial nickel wire are not a determining factor in the deterioration of the wire in service. Electrodes of nickel of relatively high purity (for commercial wire) were found to be attacked in the same manner as others of lower nickel content. Wires in which the manganese content was purposely left rather high appear to behave the same in service as those in which the minimum amount of maganese for controlling the sulphur content has been used in the metallurgical operations previous to casting. It was found possible, as described later, experimentally to reproduce the same type of deterioration in nickel wire (specimen (*f*), Table 2) in which the impurities were, in general, less than those of any of the wires which deteriorated in service.

2. OXIDATION

In order to determine the part played by oxidation in the development of the intercrystalline network of fissures by which the material is embrittled, several wires (specimen 4, Table 1) were heated at a high temperature for periods of several days. The wires were suspended in a small tube furnace of the resistance type. The ends of the tube were loosely plugged with asbestos to prevent convection air currents, which interfere in maintaining the temperature desired, but no other precautions were taken to exclude the air. (See Table 3, specimens 3*a*, 4*a*, and 12*a*.) In Fig. 13 are shown the structural changes produced by heating for 120 hours, 48 hours at approximately 750° C (740–768° C) and 72 hours at approximately 870° C (862–882° C). A very slight etching (one second in concentrated nitric acid) is necessary properly to show the changes which have occurred. The thick oxide coating which forms has a very smooth shining surface resembling varnish. It is very adherent to the metal beneath. On the inner side of this black oxide layer there is a thin film of

136076—19——2

green material. This layer, according to Burgess and Foote,[2] is probably nickelous oxide (Ni_2O), the thick outer layer being nickel oxide (NiO). In the outermost portion of the metal of the wire, immediately adjacent to the oxide layer, an intercrystalline eutecticlike network has formed. Microscopic examination at high magnification shows that this network on the inner side (i. e., toward the center of the wire) of the zone in which it has formed consists of discrete particles, probably of the nickelous oxide, which dissolve very readily in the etching fluid, leaving definite etching pits. The appearance of the granular network is that of a eutectic. Without doubt this network indicates the manner in which the oxidation progresses into the solid metal. A similar tendency of steels of a rather high nickel content to oxidize selectively along the boundaries of the crystals has been pointed out by Stead.[3]

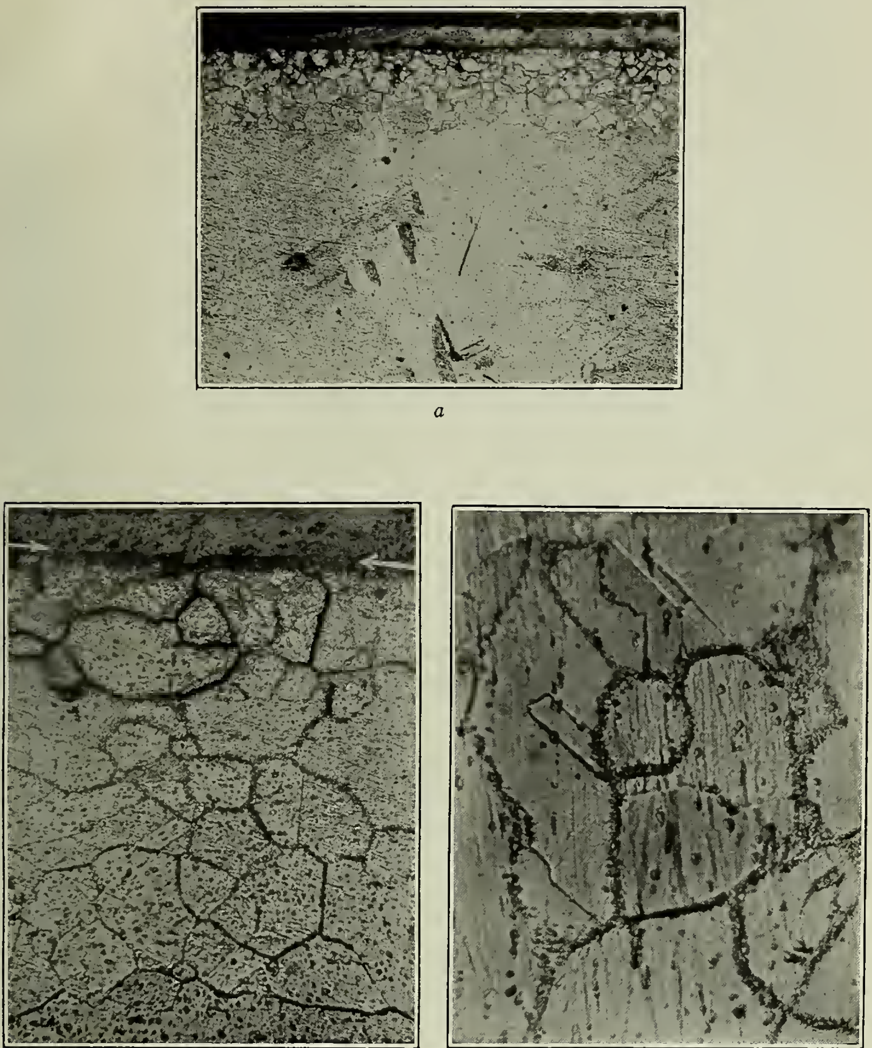
A series of heating and cooling curves were taken to illustrate the behavior at high temperatures of nickel which had been oxidized by heating for 120 hours as given above. No evidence was obtained in the behavior of the metal as recorded in the heating and cooling curves that the eutecticlike network fuses within the temperature range, 500 to 900° C, although it is formed at a temperature considerably below the upper limit given. The heating and cooling curves obtained were identical with those of the same material before oxidizing.

As the oxidation progresses, the isolated particles of the eutectic coalesce, and a continuous film is formed as is to be seen in the outer portion of the zone of the intercrystalline network (Fig. 13b). In Fig. 14 the same material is shown after deeper etching, and the appearance of the structure is identical with that of the electrodes which have deteriorated in service.

Upon long-continued heating, the width of this zone of intercrystalline network widens and a considerable embrittlement of the wire results. Long-continued heating also increases the crystal size of the metal very materially and this adds to the weakness of the overheated metal. In none of the wires which were heated was it possible to produce the definite transverse intercrystalline cracks such as were found in the deteriorated electrodes, and by which the fractures are caused. It would appear that continued heating in the presence of air at a high temperature contributes to the embrittling of the material. The effect of oxida-

[2] G. K. Burgess and P. D. Foote, Bureau of Standards, Scientific Paper No. 224, p. 53.

[3] J. E. Stead, Jour. Iron and Steel Inst., 2, p. 243; 1916.



a

b

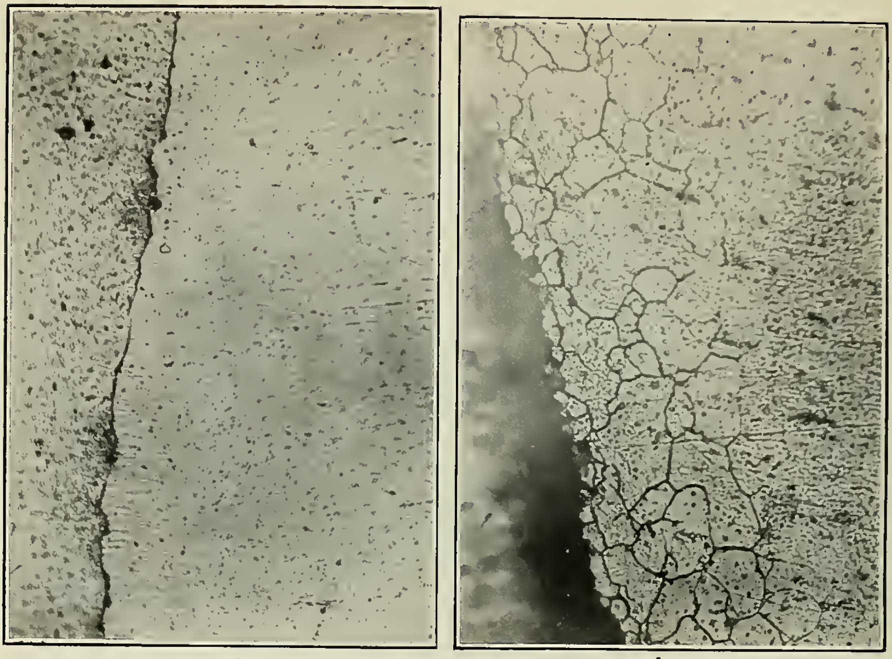
c

FIG. 14.—*Effect of oxidation upon nickel wires*

Same material as Fig. 12. Etched deeply

a, Original magnification, 100 diameters; reduced to 67 in reproduction; *b*, original magnification, 500 diameters; reduced to 385 in reproduction; *c*, original magnification, 1000 diameters; reduced to 739 in reproduction

The granular eutecticlike net work has dissolved, leaving numerous etching pits at the crystal boundaries. Etching, concentrated nitric acid, eight seconds



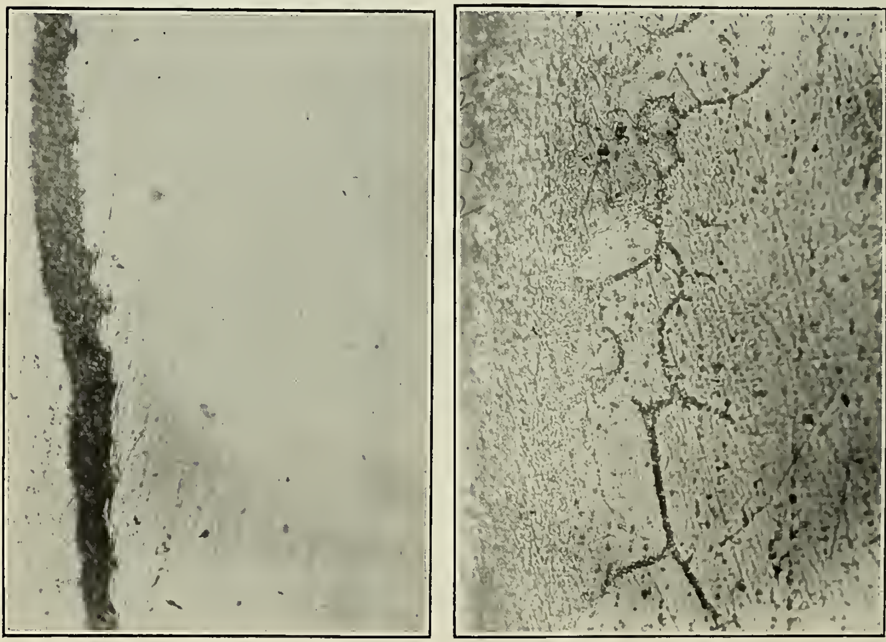
a b

FIG. 15.—*Effect of a reducing atmosphere (carbon monoxide) upon nickel wire*

The wire was heated for five hours in carbon monoxide at 720° C.

a, Cross section (unetched) of the heated portion of the wire; *b*, similar cross section; etched, concentrated nitric acid, five seconds

Original magnification, 500 diameters



a b

FIG. 16.—*Effect of a reducing atmosphere (acetylene) upon nickel wire*

The wire was heated for about three hours at 980° C; the gas was passed over the hot wire intermittently; a heavy deposit of carbon formed

a, Cross section of the heated portion of the wire unetched; a thin brittle layer, probably carbide, formed on the surface of the wire; *b*, similar cross section, etched, concentrated nitric acid, five seconds

Original magnification, 100 diameters

tion is very slight, however, compared with that of some of the other possible contributing causes, and may probably be disregarded as one of the causes of the embrittling.

3. REDUCING ATMOSPHERE

The effect of a strongly reducing atmosphere upon hot nickel wires was determined by heating wires (specimen 4, Table 1) in carbon monoxide and in acetylene. The carbon monoxide was prepared by the action of concentrated sulphuric acid upon sodium formate, and was passed through soda lime to remove any carbon dioxide which might be present. Carpenter and Smith have shown that carbon dioxide in any appreciable amount will inhibit the carburization of iron by means of carbon monoxide.[4]

The effect of carbon monoxide was determined at two different temperatures; in the first case (710° C) the gas was passed at a very slow rate continuously over the wire which was contained in a long silica tube heated (electrically) at the center. The wire was heated for five hours. In the second case the furnace was maintained at 980° C and the gas was passed intermittently, the furnace being tightly closed at both ends when the gas was not passing. The specimen was exposed to the hot gas for four hours. In both cases carbon dioxide was produced as was shown by the escaping gas as it bubbled through barium hydroxide, but no pronounced deposit of carbon on the wire was produced. The effect of the gas upon the nickel is essentially the same in the two cases. Fig. 15, *a* and *b*, shows the appearance after the treatment. No change was apparent in the unetched state; slight etching reveals a thin surface layer in which the intercrystalline fissures are well developed.

The specimen which was exposed to acetylene was heated at 980° C for approximately three hours. A very heavy deposit of carbon was produced in this case, and it was not possible to pass the gas through continuously. The surface of the wire became coated with a thin black brittle coating which flaked off on slight bending leaving the surface roughened. Undoubtedly this layer is a carbide. Fig. 16, *a* and *b*, shows the change produced in the wire by the hot acetylene. The wires were still ductile after heating, in both cases, and gave no evidence of pronounced brittleness upon bending.

The effect of the hot reducing gases appears to be somewhat greater than that of an oxidizing atmosphere, although the method of attack is the same in each case; that is, intercrystalline. No

[4] H. C. H. Carpenter and C. C. Smith, Reaction Between Carbon Monoxide and Electrolitic Iron, Jour. I. and S. Inst., 98, p. 139; 1918.

indications of localized action which might result in deep transverse cracks in the wire were observed in any of the wires exposed to the reducing gases; the metal is uniformly affected at the exposed surface.

4. INTENSE LOCAL HEATING

In general, the effect of the electric spark upon the electrode must be regarded as an intense local overheating. Two nickel wires (specimen 4, Table 1) were used as electrodes, and sparks were passed between them. The sparks were produced by breaking the secondary circuit of a transformer (an electric stylograph, used for writing on metals, was used). The current in the secondary winding could be varied from approximately 145 amperes to 400. These conditions, of course, are not comparable with the ignition system of a gas engine. It was not attempted to duplicate service conditions, but rather to accelerate the action. The aim, however, was to heat the metal strongly in a very small area while the remainder remained relatively cool. Specimens were prepared by sparking in air and also in an atmosphere of carbon dioxide, in order that oxidation might be reduced to a minimum. The results obtained in both cases were of the same general character.

In Fig. 17 is shown the appearance of a spot produced by a relatively weak spark. The portion which has been heated strongly is sharply differentiated from the metal which remained rather cool. A network of intercrystalline cracks has broken up the continuity of the overheated metal; these extend for some distance into the surrounding sound metal as intercrystalline fissures.

A much larger overheated area is shown in Fig. 18. This specimen was "sparked" in an atmosphere of carbon dioxide, a much heavier current being used. Three zones are to be noted. An outer one in which the metal was fused, an intermediate one which was strongly overheated and developed the network of intercrystalline fissures, and the inner or relatively cool metal which is unchanged for the most part except for the intercrystalline cracks of the overheated zone which extend into it. The distinct dentritic pattern of the metal in the outer zone is proof that the metal here has solidified from the molten state with the production of this characteristic structural pattern. The line of demarcation between the overheated (but not melted) metal and the relatively cool portion is a very definite one. The intercrystalline cracks have, however, extended into the sound metal of the interior; they are truly intercrystalline in their course.

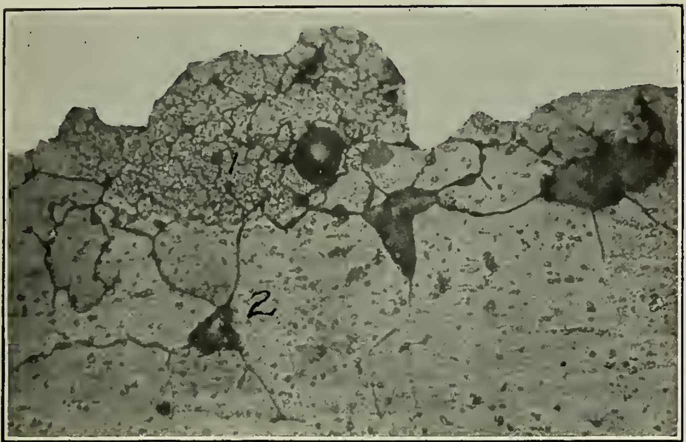
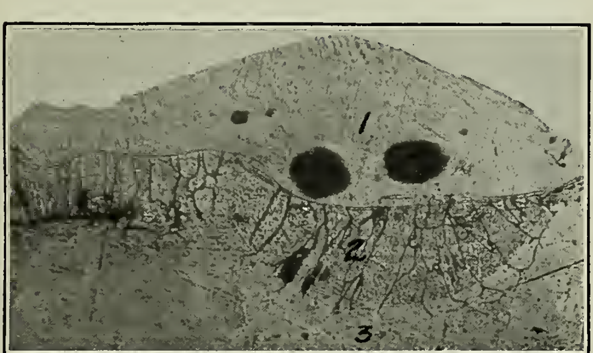


FIG. 17.—*Effect of intense local heating upon nickel wire: Longitudinal section through a spot produced upon the surface of a nickel wire by means of an electric spark*

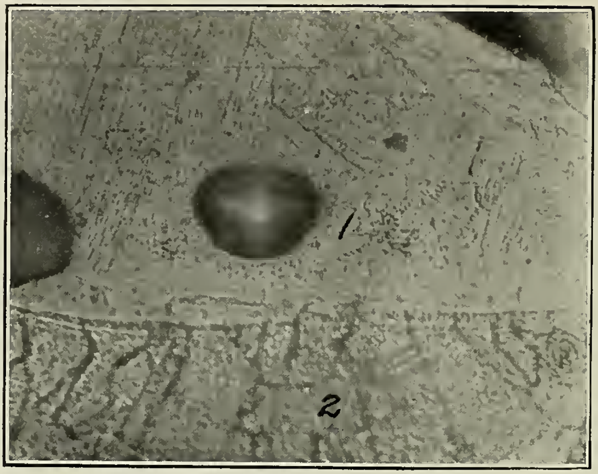
In zone 1, the metal has been highly heated the intercrystalline network has resulted. This network extends into zone 2, the sound metal which has remained relatively cool. Magnification, 500 diameters. Etching, concentrated nitric acid, three seconds.



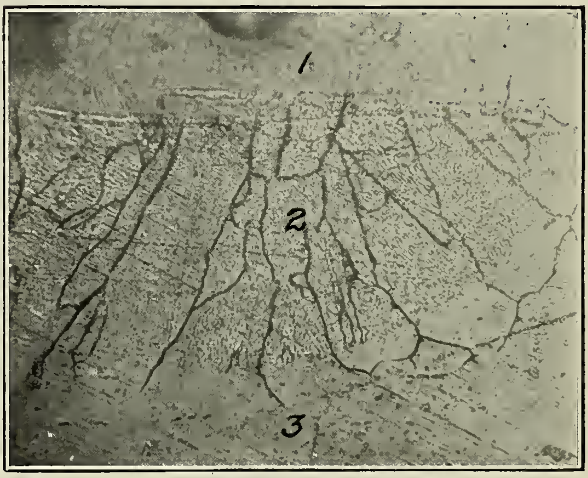
a

FIG. 18.—*Effect of intense local heating upon nickel wire: Longitudinal section through a spot produced upon the surface of a nickel wire by the electric spark in an atmosphere of carbon dioxide*

a, Magnification, 100 diameters; three distinct zones are seen



b



c

FIG. 18 (*continued*).—*Effect of intense local heating upon nickel wire: Longitudinal section through a spot produced upon the surfae of a nickel wire by the electric spark in an atmosphere of carbon dioxide*

b, Magnification, 500 diameters, zone 1 of *a*. The metal has been melted and upon solidification produced the characteristic dentritic structure; *c*, magnification, 500 diameters, zone 2 of *a*. The metal has been highly heated but not melted. The intercrystalline network has been produced; this extends for some distance into zone 3 of *a*—the sound metal which remained relatively cool

In none of the wires which were heated by the electric spark could any of the definite transverse cracks be found, although in some cases the effect of as many as 25 to 30 sparks was concentrated in a narrow ring around the wire. The intercrystalline network produced by the local heating by the electric spark properly are to be regarded as a heat effect only, and are not accompanied by oxidation, except in the outermost surface of those produced in air.

5. INFLUENCE OF COMBINED ACTION OF TENSIONAL STRESS AND HEAT

In order to explain the formation of the definite transverse cracks which form in the side electrodes, a series of wires (specimen 4, Table 1) were stressed in tension while heated at a high temperature. No attempt was made to reproduce the temperature of the electrode in service since no accurate measurement can be made of the temperature of the small spot at which the spark occurs. The measured temperature of the electrode would be considerably below the actual temperature at this spot. The temperatures used below and elsewhere are considerably above the average temperature of the electrode. The work of Rosenhain and Ewen[5] has shown that the fracture produced in metals which are broken in tension while hot is always intercrystalline in its course. The samples of wire tested were about 2 feet in length; the specimen was inserted through a small vertical tube furnace of the resistance type, firmly attached to a support above and loaded with a weight below. Only the central portion of the wire was heated; in all cases the break took place within this heated portion. The results are summarized in Table 3.

The stress necessary to produce fracture in the hot wire is very small compared with the ultimate strength of the material at ordinary temperatures (approximately 5 per cent). The appearance of the fracture is very characteristic—a sharp crystalline break with no appreciable elongation or reduction of cross-sectional area. A series of small transverse cracks, parallel and close to the face of the break, is usually to be found. Fig. 19 shows the appearance of two of the wires broken in this manner, and shows the characteristic features of the fracture.

[5] W. Rosenhain and D. Ewen, Intercrystalline Cohesion in Metals, Collected Researches, 10 and 11, National Physical Laboratory, Teddington.

TABLE 3.—Combined Effect of Heat and Stress on Nickel Wires

[Ultimate strength of wire, 65 000 pounds per square inch; elongation in 2 inches, 28 per cent; diameter of wire, 0.073 inch.]

Specimen	Average temperature	Load	Result and Remarks
	°C	Lbs./in²	
1	942	3300	Wire put in cold furnace; gradually heated; broke in 3 hours.
2	970	3800	Put in cold furnace; gradually heated; broke in 3 hours, 50 minutes.
3	940	3300	Put into hot furnace; broke in 20 minutes.
3a	940	No. load.	Heated continuously for 72 hours.[a]
4	940	3800	Put into hot furnace; broke in 20 minutes.
4a	940	No load.	Heated continuously for 72 hours.[a]
5	988	3800	Put into hot furnace; broke in 10 minutes.
6	993	3300	Put into hot furnace; broke in 13 minutes.
7	993	3500	Put into hot furnace; broke in 12 minutes.
8	1004	3300	Put into hot furnace; broke in 13 minutes.
9	1020	3300	Put into warm furnace; heated rapidly to temperature; wire broke in 30 minutes.
10	1100	1180	Wire broke; time not determined as wire broke during night.
11	740	1180	Heated 72 hours; wire did not break.[a]
12	740 880	1180	48 hours at lower temperature, 72 hours at higher; wire did not break.[a]
12a	740 880	No load.	48 hours at lower temperature, 72 hours at higher.[a]

[a] Microexamination showed the beginning of an intercrystalline network in the surface metal.

The changes in the microstructure which are produced by the combined action of tensional stress and heat are shown in Fig. 20. A network of fine intercrystalline fissures with numerous transverse cracks extending into the body of the wire is produced. In Fig. 21 a section through the end of one of the fractured wires is shown. The fracture is distinctly intercrystalline, and has resulted from the formation of transverse intercrystalline cracks which are identical in appearance with those which are found in the electrodes which deteriorated in service.

The brittleness of metals at high temperatures has been explained by Rosenhain and Ewen[6] as due to the weakening of the intercrystalline "amorphous cement" upon heating. The behavior of nickel is very similiar to that of lead, tin, and the other metals of relatively low melting point, which were used in the work of Rosenhain referred to above. Nickel differs, however, in one important respect, in that the intercrystalline weakness becomes manifest at temperatures far below the melting point. Metals such as tin, lead, and aluminum must be heated to within a few degrees of the melting point in order to demonstrate this

[6] Loc. cit.

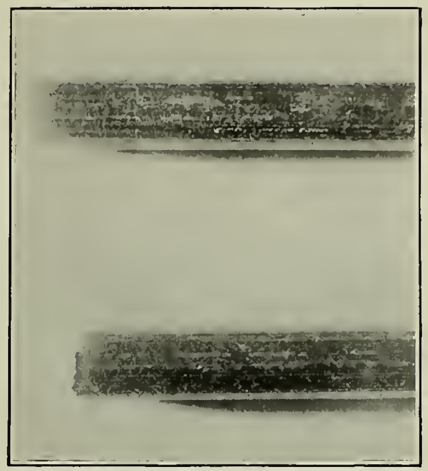
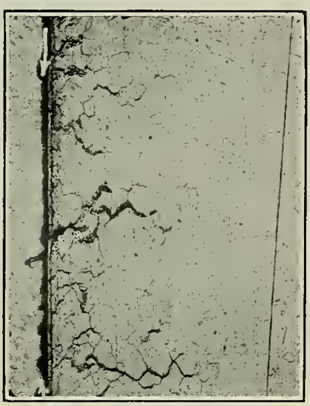


FIG. 19.—*Combined effect of heat and tensional stress upon nickel wires*

Fractured ends of two nickel wires broken in tension while hot. Magnification, 5 diameters

a



b

FIG. 20.—*Combined effect of heat and tensional stress upon nickel wire: Longitudinal section of a nickel wire stressed in tension while hot until fracture occurred. The arrows indicate the edge of the section*

a, Unetched; *b*, etched, concentrated nitric acid, three seconds
Original magnification, 100 diameters; reduced to 53 in reproduction

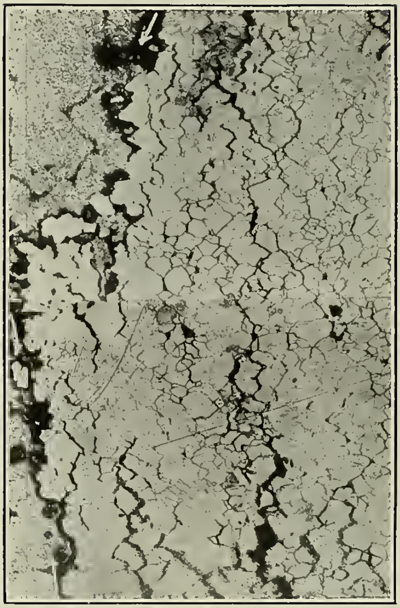


FIG. 21.—*Combined effect of heat and tensional stress upon nickel wire: Longitudinal section through the fracture produced in a hot wire under constant load*

The fracture is distinctly intercrystalline and identical in appearance to those produced in service. The arrows indicate the face of the fracture, the micrograph shows the entire section of the wire. Original magnification, 100 diameters; reduced to 53 in reproduction. Etching, concentrated nitric acid, three seconds

intercrystalline weakness. Nickel also differs markedly from iron in its behavior at high temperatures. Rosenhain and Humphrey [7] demonstrated that iron and mild steel will break under a relatively very low stress at high temperatures with an intercrystalline break but with a very pronounced elongation, often more than 100 per cent. Nickel breaks with no elongation.

IV. EXPLANATION OF SERVICE DETERIORATION OF ELECTRODES

The types of deterioration of the nickel wires in service as spark-plug electrodes described above are to be attributed to the combined effect of several causes.

The surface layer of wires heated continously in a reducing atmosphere shows evidence of intercrystalline brittleness. This behavior of nickel is in agreement with the fact that deterioration in service begins at the surface and progresses inward. Prolonged heating in the air will, likewise, develop brittleness in the outer layer by the formation of an intercrystalline eutecticlike network. This effect is very slight, however, in comparison with other causes and, probably, does not affect materially the rate of deterioration of the wires. The increased crystal size due to prolonged heating will contribute somewhat to the failure of the wires by facilitating the formation of the transverse intercrystalline fissures.

Local overheating by the electric spark (with the subsequent cooling) gives rise to the definite intercrystalline fissures in such overheated areas which contribute to the local brittleness of the wire. The more rapid wearing away of the metal on the side exposed to the spark, probably, is due to this. The weakening of the "intercrystalline cement" upon heating, and the pronounced intergranular separation which occurs upon application of a very low stress, is, probably, however, responsible for the definite "knife-cut" fractures which occur in some of the electrodes. Such stresses may be due to the effect of unequal heating and cooling of the wire, to the vibratory and explosive action of the spark, and to the constant jarring and vibration of the engine as a whole in service, this being particularly pronounced in the case of airplane motors. The stressing of the side electrodes firmly anchored at both ends by the differential expansion of the shell of the plug is probably, however, the most potent source of danger to which such electrodes are exposed. The other possible stresses cited affect all electrodes, and, probably, aid materially

[7] W. Rosenhain and J. W. C. Humphrey, Collected Researches, 11, National Physical Laboratory, Teddington.

in the formation of the intercrystalline network which always is formed and by which the wire is embrittled.

V. SUMMARY

1. The service deterioration of nickel spark-plug electrodes is shown to be due to an intercrystalline embrittlement of the wire. The cohesion between the grains is so lessened that a network of intercrystalline fissures is formed, and also, under certain conditions, well-defined transverse cracks which extend deeply into the wire.

2. Variation in chemical composition of the nickel wires does not appear to have much bearing on the deterioration; the latter occurs in wire of relatively high purity as well as in the "97-per cent grade" usually specified.

3. Continued heating of nickel wire in the air at a high temperature contributes slightly to the embrittlement of the wire by the formation of an intercrystalline eutecticlike oxide network. This, however, is probably negligible in the deterioration of the electrodes in service.

4. Nickel wires heated in a strongly reducing atmosphere show evidence of an intercrystalline embrittlement of the surface metal. A thin brittle surface skin, apparently carbide, forms in case considerable carbon is deposited upon the wire.

5. Intense local heating by means of the electric spark, together with the sudden cooling, contributes to the embrittling of the wire by the formation of fine intercrystalline fissures in the small overheated zone.

6. The mechanical properties of nickel wire at high temperatures are very different from the properties as ordinarily measured. The application of a relatively low stress to the hot wire is sufficient to fracture the wire by the formation of transverse intercrystalline cracks. The tensional stress due to the differential expansion of the shell and the electrodes is probably sufficient to cause the formation of the transverse breaks in those electrodes which are anchored firmly at both ends. Such cracks were not found in other forms of nickel electrodes.

The chemical analyses of the material were made by J. A. Sherrer, the mechanical tests by R. W. Woodward, and the thermal analysis by H. Scott. Much credit is due J. F. T. Berliner for the very careful work done in the preparation of the sections for metallographic examination.

Washington, May 23, 1919.